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VIBRATIONAL RELAXATION OF HF(V = 1, 2, AND 3) IN H2, N2, AND CO--ETC(U)

SEP 76   J F BOTT   F04701-75-C-0076

UNCLASSIFIED   TR-0076(6603)-10   SAMSO-TR-76-208   NL

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Aerophysics Laboratory
Laboratory Operations
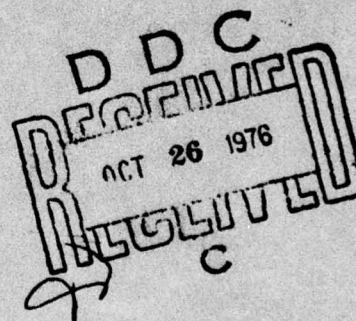The Aerospace Corporation
El Segundo, Calif. 90245

30 September 1976

Interim Report

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Prepared for

AIR FORCE WEAPONS LABORATORY
Kirtland Air Force Base, N. Mex. 87117

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This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract F04701-75-C-0076 with the Space and Missile Systems Organization, Deputy for Advanced Space Programs, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by W. R. Warren, Director, Aerophysics Laboratory. Lieutenant Ronald C. Lawson, SAMSO/YAPT, the project engineer.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

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FOR THE COMMANDER

Ronald C. Lawson, 1st Lt, USAF
Technology Plans Division
Deputy for Advanced Technology

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SAMSO-TR-76-208	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* VIBRATIONAL RELAXATION OF HF(v = 1, 2, AND 3) IN H_2, N_2, AND CO_2.		5. TYPE OF REPORT & PERIOD COVERED Interim rept.
		6. PERFORMING ORG. REPORT NUMBER TR-0076(6603)-10
7. AUTHOR(s) Jerry F. Bott		8. CONTRACT OR GRANT NUMBER(s) F04701-75-C-0076
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, Calif. 90245		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Weapons Laboratory Kirtland AFB, N. Mex. 87117		12. REPORT DATE 30 September 1976
		13. NUMBER OF PAGES 37
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)* Space and Missile Systems Organization Air Force Systems Command Los Angeles, Calif. 90009	39p.	15. SECURITY CLASS. *(of this report)* Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

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18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Chemical kinetics
Chemical laser
HF
Laser-induced fluorescence

Vibrational relaxation

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The vibrational relaxation times of HF(v = 1, 2, and 3) were measured in H_2, N_2, and CO_2 by a laser-induced fluorescence technique. The upper vibrational levels were produced by sequential absorption in which HF(v = 0) was pumped first to HF(v = 1) and subsequently to HF(v = 2) and HF(v = 3) by photons from a pulsed multiline HF chemical laser. At T = 295 K, the relaxation rates of HF(v = 1), HF(v = 2), and HF(v = 3) in H_2 were found to be, respectively, $(1.43 \pm 0.15) \times 10^{-2}$, $(1.23 \pm 0.1) \times 10^{-2}$, and (1.13 ± 0.1)

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19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

$\times 10^{-2}$ μsec-Torr^{-1}; in N_2, $(1.45 \pm 0.15) \times 10^{-4}$, $(8.1 \pm 1.0) \times 10^{-4}$, and $(2.92 \pm 0.3) \times 10^{-3}$ μsec-Torr^{-1}; and, in CO_2, 0.039 ± 0.004, 0.19 ± 0.02, and 0.38 ± 0.04 μsec-Torr^{-1}. Values of $(7.5 \pm 1) \times 10^{-4}$ and 0.4 ± 0.04 μsec-Torr^{-1} were obtained for the relaxation rates of HF($v = 3$) in O_2 and HCl, respectively.

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I. INTRODUCTION

During the past few years, the vibrational relaxation of HF(v = 1) has been studied for a large number of collision partners over a large range of temperatures.[1-3] These studies were undertaken because of the recent interest in theories of vibrational energy transfer and the development of the HF chemical laser. Vibrational-relaxation measurements have been largely confined to HF(v = 1) because of the difficulties involved in the controlled production of the higher levels under circumstances in which specific upper level processes can be isolated. In the few studies of upper vibrational level deactivation, the techniques of direct laser pumping of the second vibrational level,[4] low-pressure combustion with spectroscopic diagnostics,[5] reactive flows in medium-pressure flow tubes,[6-8] and laser-induced fluorescence by sequential absorption[9,10] were used. Laser-induced fluorescence was employed in this study. This technique had been used previously by Osgood, Sackett, and Javan[9] in their study of the deactivation of HF(v = 2, 3, and 4) by collisions with HF and by Hinchen[10] to study the vibrational energy transfer from DF(v = 1 and 2) to CO_2.

A knowledge of the upper level deactivation rates is important for understanding and modeling the performance of the HF chemical laser since the pumping reaction

$$F + H_2 \rightleftharpoons HF(v) + H \tag{1}$$

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directly populates $v = 1$, 2, and 3. Theoretical calculations of these rates have been made for only a few cases,[11] e.g., the V-V exchange between $HF(v)$, $DF(v)$, and CO_2. Few comparisons of theoretical and experimental results have been made because such calculations are difficult and because experiments for measuring and interpreting these rates are difficult to design. The laser-induced fluorescence experiment in which sequential absorption of photons produces the higher excited levels is relatively easy to perform, and the interpretation of the data is straightforward. The experiments can be performed for a large ratio of the collision partner to HF, thereby reducing the HF-HF V-V deactivation processes to negligible contributions. This technique has been used in the present study to measure the vibrational relaxation rates of $HF(v = 1, 2, \text{ and } 3)$ in H_2, N_2, and CO_2 and of $HF(v = 3)$ in O_2 and HCl.

II. EXPERIMENTAL

The experimental arrangement is shown in Fig. 1; the apparatus includes an HF TEA laser, a fluorescence cell, and several detectors. Because of its availability and for convenience, a 10-m-long, 16.5-cm-diameter shock tube was used as the fluorescence cell. The shock tube and gas handling system has been used for a number of temperature-dependence studies of HF($v = 1$) and HCl ($v = 1$) vibrational relaxation. [12, 13]

The TEA laser described in Ref. 13 was used with the SF_6 and H_2 flow regulated to a total pressure of about 35 Torr. An H_2 partial fraction of 0.095 was used for the experiments in which HF($v = 3$) was produced by sequential absorption. The laser was detuned by reducing the H_2 partial fraction to 0.005 when only HF($v = 1$) and HF($v = 2$) were to be produced. The total energy in the laser pulse was estimated to be 1 to 2 mJ on the basis of previously calibrated lasers. [12] The duration of these laser pulses is typically 100 to 300 nsec. The laser can be operated at a repetition rate of ~3 Hz without substantial degradation of the signal. A 5.08-cm Au-coated mirror with a 12.5-m radius and a 1.27-cm-diameter sapphire window mounted in the shock tube formed the optical cavity. A shorter 70-cm laser also produced direct pumping of HF($v = 3$) but in smaller concentrations by a factor of 2.5.

The fluorescence from HF($v = 3$) was monitored with an RCA C-31034 GaAs photomultipler. A Kodak 87C wratten filter and the spectral sensitivity of the photomultiplier limited the detected fluorescence to wavelengths between
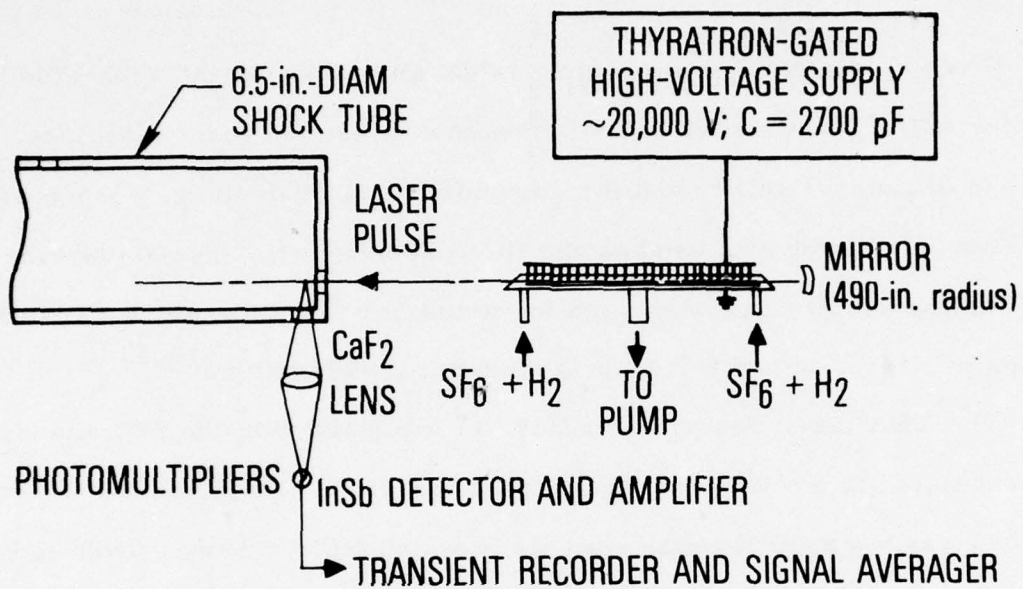
Fig. 1. Experimental Apparatus.

8000 and 9000 Å. An RCA 7102 photomultiplier with an Si filter was used to follow the HF first overtone at $\lambda \sim 1.26\ \mu m$. The photomultipliers simply were placed against the observation window for the respective measurements. A Texas Instruments InSb IR detector was used to monitor the HF(v = 1) fluorescence, which was focused onto the detector with a 5.08-cm-diameter CaF_2 lens having a 15-cm focal length. The InSb signal was amplified with a Perry Associates Model 050 amplifier. The combined response time was $<1.4\ \mu sec$. Likewise, the response time of the photomultipliers (1-kΩ load resistors) was $<1\ \mu sec$. The signals from the IR detector or photomultipliers were recorded with a Biomation Model 805 transient recorder and transferred to a Nicolet Model 1072 signal averager, where 32 to 512 experiments were stored and averaged before being displayed on an X-Y recorder. Because of the high sensitivity of the GaAs photomultiplier, the HF(v = 3) fluorescence was recorded with the best signal-to-noise ratios. A single fluorescence trace is shown in Fig. 2.

The amount of HF pumped to the various levels was not measured. However, the ratio of HF(v = 3) to HF(v = 2) was estimated to be ~ 0.1 on the basis of the estimated photomultiplier sensitivities at the two wavelengths,[14] $S_{1.26\mu m}/S_{0.89\mu m} \sim 10^{-3}$, and the ratio of the radiative lifetimes of the two levels $\tau_{3\to 0}/\tau_{2\to 0} \sim 20$. The HF(v = 3) measurements were not complicated by $4 \to 1$ fluorescence; no HF(v = 4) was produced by the multiphoton absorption since the laser does not operate on the $4 \to 3$ transition. Indeed, no third overtone fluorescence was detectable. For the measurements of HF(v = 2) deactivation, the laser was detuned so that no HF(v = 3) was pumped directly.

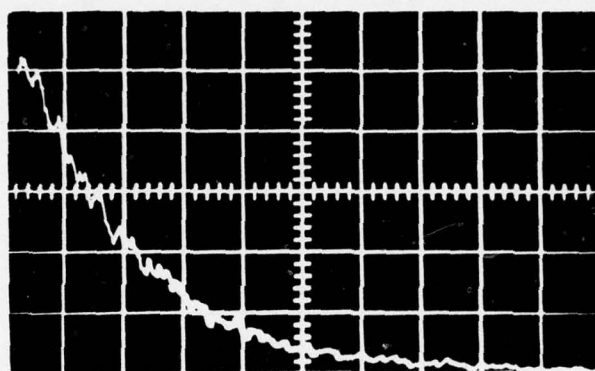Fig. 2. Single Fluorescence Trace for
HF(v = 3). (Pressure = 20
Torr; 0.02% HF, 20% H_2,
Balance Ar; Vertical Scale =
10 mV/cm, Horizontal Scale =
10 μsec/cm).

The HF(v = 2) data did not appear to be affected by the tuning or detuning of the laser, which was consistent with the estimate of the relative populations of v = 3 and v = 2 and also their different decay times. At 20-Torr total pressure, the measured intensity of HF(v = 3) was linear between HF concentrations of 0.02 and 0.1%, indicating that the medium was optically thin and that there were no collisional effects during the laser pulse. The initial intensity of the HF(v = 3) fluorescence is shown in Fig. 3 for gas mixtures at 20 Torr containing 0.02% HF and various proportions of H_2. The initial intensity was independent of the H_2 concentration, although the decay times ranged from about 4 to >100 μsec. The shortest decay time, 4 μsec, was still long compared to the 100 to 300 nsec laser duration.

Gases used in the experiments included 99.999% Ar, 99.999% H_2, 99.9% HF (liquid phase), and 99.999% N_2 from Matheson Gas Products Co. The 99.9% CO_2 was from Liquid Carbonics. The Ar, H_2, N_2, and CO_2 were used from the bottle; the HF was distilled by cooling to 77 K, pumping away the residual gases, and then warming to a temperature at which its vapor pressure was about 30 Torr. The gas mixtures were prepared in a stainless-steel mix tank with the major gas component injected through a supersonic orifice in order to provide good mixing.
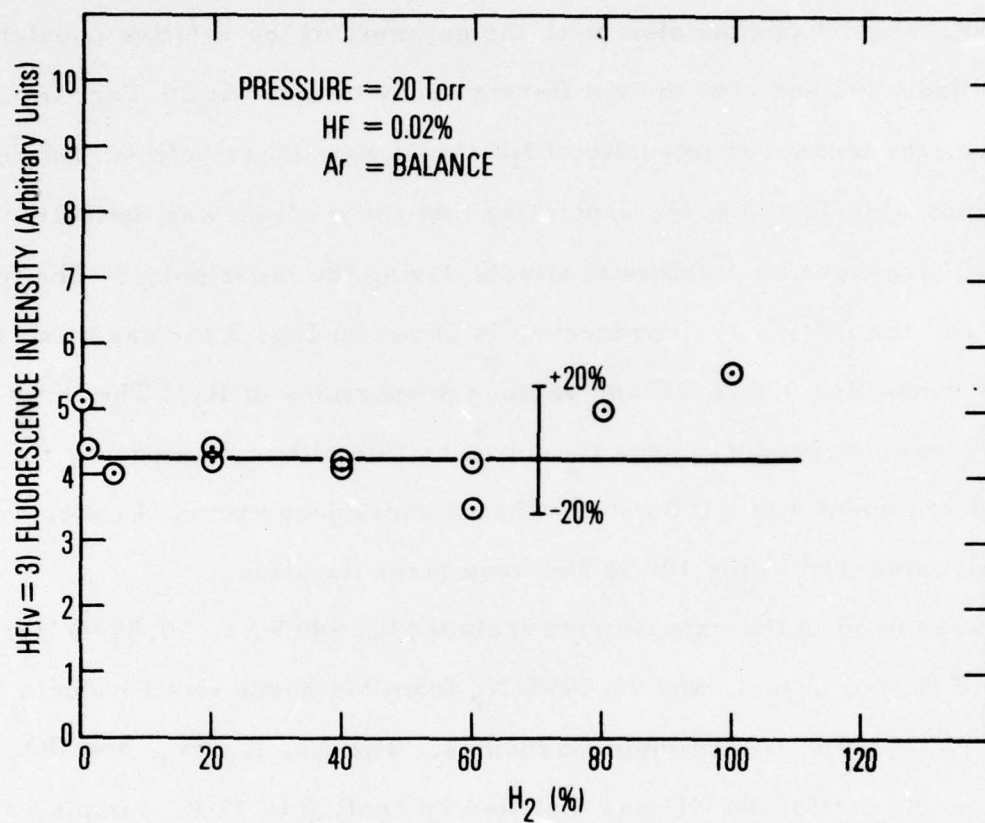
PRESSURE = 20 Torr
HF = 0.02%
Ar = BALANCE

HF(v = 3) FLUORESCENCE INTENSITY (Arbitrary Units)

+20%
−20%

H_2 (%)

Fig. 3. Initial HF(v = 3) Fluorescence Intensity
Versus Percentage H_2

III. RESULTS

A. VIBRATIONAL RELAXATION OF HF(v = 1, 2, AND 3) IN H_2

The relaxation rates of HF(v = 3) and HF(v = 2) were measured in gas mixtures containing 0.02% HF and various proportions of H_2 and Ar at a total pressure of 20 Torr. The exponential decay times obtained from semilog plots of the intensities were multiplied by the total pressure, and the reciprocal values of P_T were plotted (Figs. 4 and 5) versus percentage H_2. Relaxation rates for HF(v = 1) were obtained with mixtures containing 0.1% HF (Fig. 6). When HF molecules are excited to the first vibrational level in H_2, the HF(v = 1) population initially decreases primarily by the V-V exchange with H_2.

$$HF(v = 1) + H_2(v = 0) \overset{k_2^{vv}}{\rightleftharpoons} HF(v = 0) + H_2(v = 1) \tag{2}$$
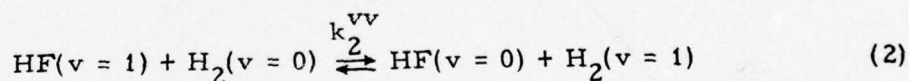
At longer times, the coupled populations of HF(v = 1) and H_2(v = 1) are deactivated by the slower V-R, T processes, including

$$HF(v = 1) + H_2(v = 0) \overset{k_3^{vr}}{\longrightarrow} HF(v = 0) + H_2(v = 0) \tag{3}$$
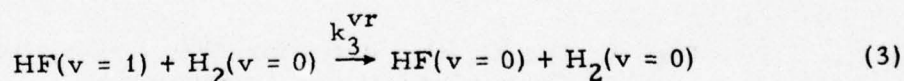
The equations describing this relaxation process are given in Refs. 12 and 15. Because of the small concentrations of HF relative to H_2, only single exponential decays were observed. For the conditions of the experiment, the total deactivation rate $(k_2^{vv} + k_3^{vr})$ was proportional to the slope of the data

PRESSURE = 20 Torr
HF = 0.02%
Ar = BALANCE

$(P\tau^{-1}) \times 10^3$ (μsec-Torr^{-1})

$k_{HF(3)-H_2} = (11.3 \pm 1.0) \times 10^{-3}$ μsec-Torr^{-1}

H_2 (%)
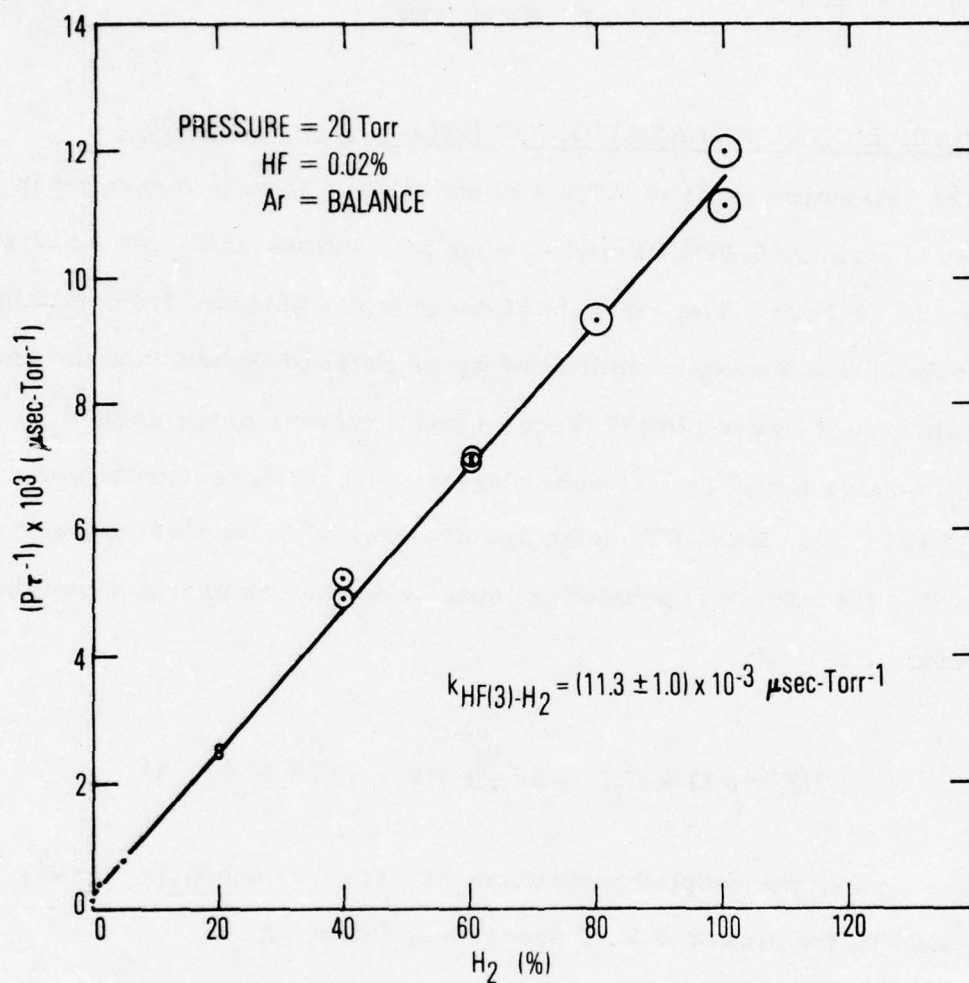
Fig. 4. Deactivation Rates for HF(v = 3) in Mixtures
Containing Various Amounts of H_2

Fig. 5. Deactivation Rates for HF(v = 2) in Mixtures
Containing Various Amounts of H_2

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PRESSURE = 20 Torr

HF = 0.1%

$(P\tau)^{-1} \times 10^3$ (sec-Torr^{-1})

7

6

5

4

3

2

$k = (1.43 \pm 0.15) \times 10^{-2}$ μsec-Torr^{-1}

1

0

0   10   20   30   40   50   60

H_2 (%)
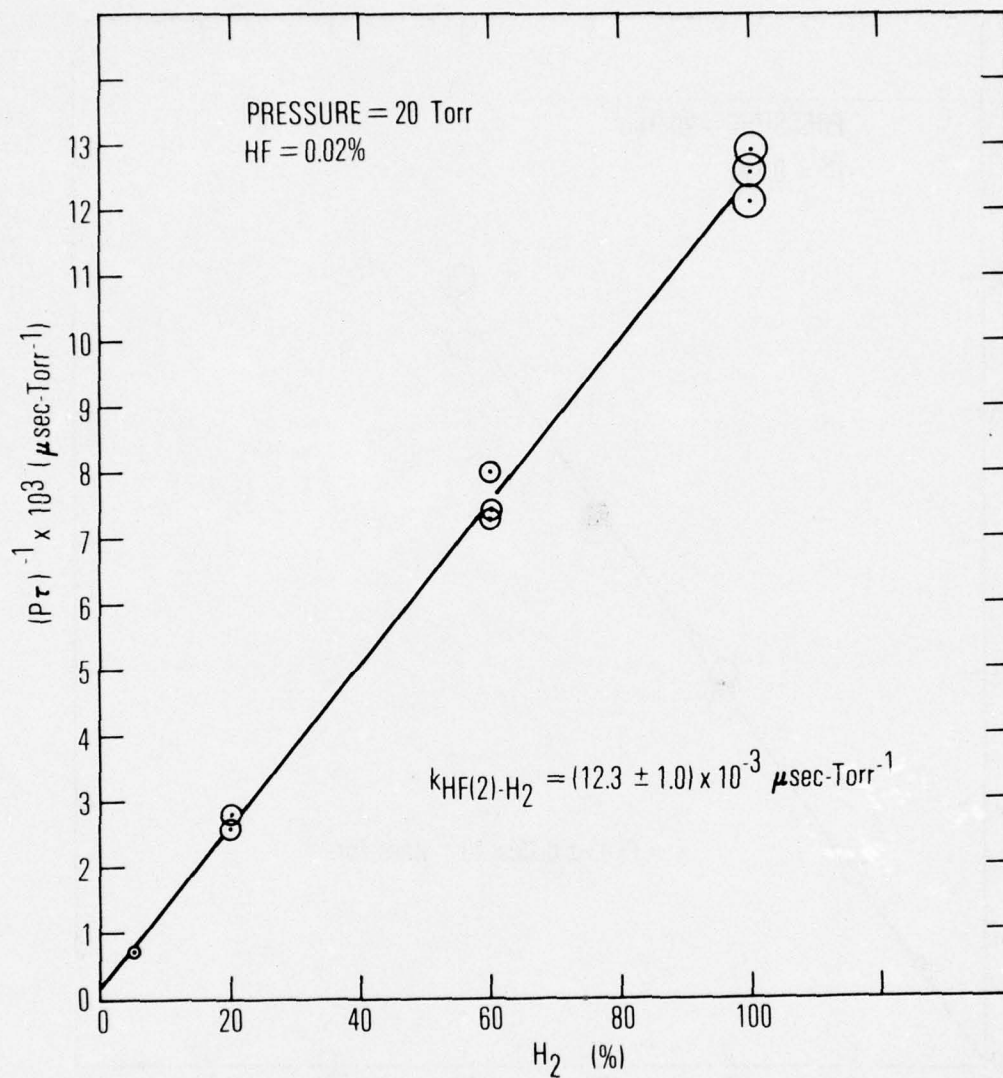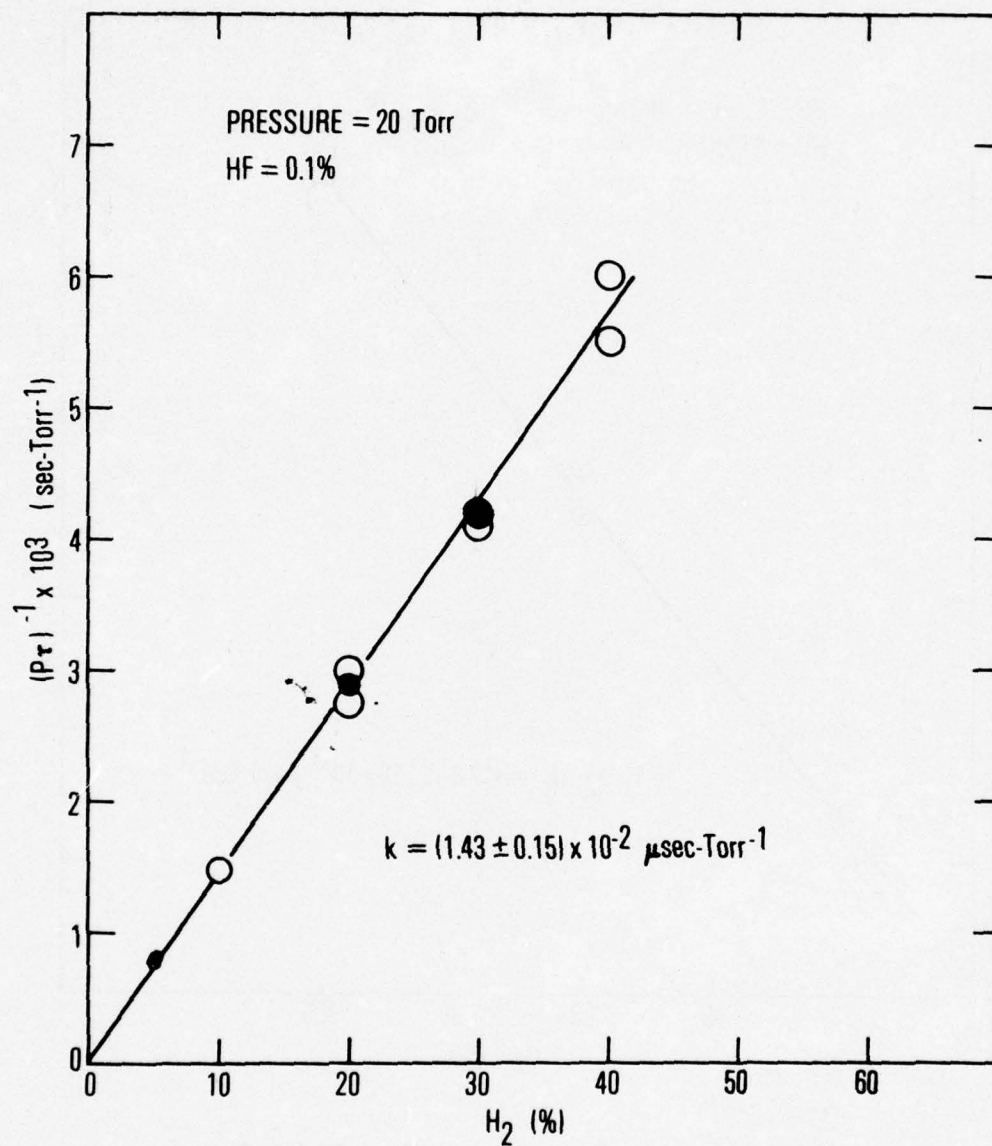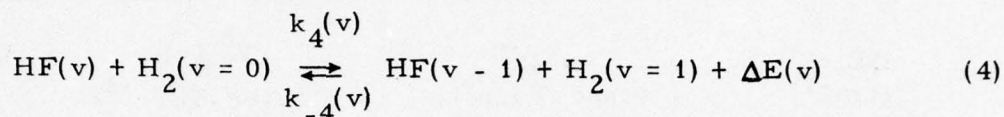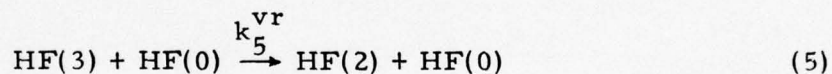
Fig. 6. Deactivation Rates for HF(v = 1) in Mixtures
Containing Various Amounts of H_2

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in Fig. 6; k_3^{vr} was a small contribution.[16] The second and third vibrational levels were removed by H_2, most probably by the V-V exchange

$$HF(v) + H_2(v = 0) \overset{k_4(v)}{\underset{k_{-4}(v)}{\rightleftarrows}} HF(v - 1) + H_2(v = 1) + \Delta E(v) \tag{4}$$

although the possibility of multiquantum exchanges can not be excluded. The relaxation rates obtained from the slopes of the data are listed in Table I and are in the ratio of 1, 0.86, and 0.79 for $v = 1$, 2, and 3, respectively. Note that if the HF vibrational levels had been coupled together by $HF(v)$-HF V-V exchanges, the rates would have been in the ratio of 1, 2, and 3, respectively.

With no H_2 present in the gas mixture, the $HF(v = 3)$ was deactivated by collisions with HF itself in such V-R, T and V-V processes as

$$HF(3) + HF(0) \overset{k_5^{vr}}{\rightarrow} HF(2) + HF(0) \tag{5}$$

and

$$HF(3) + HF(0) \overset{k_6^{vv}}{\rightleftarrows} HF(2) + HF(1) \tag{6}$$
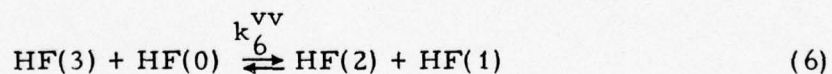
Depending on the initial relative concentrations of the HF(0), HF(1), HF(2), and HF(3), the V-V exchange, Reaction (6), can either produce or remove HF(3) on balance. However, after their initial fast rise during the laser pumping, the fluorescence traces decayed monotonically with no apparent V-V pumping from lower levels. After its initial excitation, the decay rate of HF(3) can be described by

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TABLE I.   MEASURED RATES FOR THE DEACTIVATION OF HF(v)

$$\text{PRIMARILY } HF(v) + H_2(0) \underset{k_{-4}(v)}{\overset{k_4(v)}{\rightleftharpoons}} HF(v-1) + H_2(1) + \Delta E(v)$$

v	$\Delta E(v)^a$ (cm^{-1})	$k_4(v)$ $(\mu sec\text{-}Torr^{-1})$	$k_{-4}^b(v)$ $(\mu sec\text{-}Torr^{-1})$	$k_{-4}(v)/k_{-4}(1)$
1	-201	$(1.43 \pm 0.15) \times 10^{-2}$	3.8×10^{-2}	1
2	-367	$(1.23 \pm 0.1) \times 10^{-2}$	7.3×10^{-2}	1.9
3	-535	$(1.13 \pm 0.1) \times 10^{-2}$	15.3×10^{-2}	4.0

[a]Calculated with all molecules assumed to be in the $J = 0$ rotational level.

[b]$k_{-4}(v) = k_4(v) \exp[1.435 \, \Delta E(v)/T]$

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$$\frac{d[HF(3)]}{[HF(3)]\,dt} = -\left(k_5^{vr} + k_6^{vv}\right)[HF(0)] + k_{-6}^{vv}\,\frac{[HF(2)]\,[HF(1)]}{[HF(3)]} \qquad (7)$$

The monatomic decay of the HF(3) fluorescence indicates that the first term on the right-hand side was always greater than the second term. When H_2 was present in the gas mixture, the importance of the second term was further decreased since H_2 was found to deactivate HF(2) and HF(1) faster than [HF(3)]. The decay rate of HF(3) can be approximated then with

$$\frac{d[HF(3)]}{[HF(3)]\,dt} = -\left(k_5^{vr} + k_6^{vv}\right)[HF(0)] + k_4(3)[H_2(0)] \qquad (8)$$

Indeed, the extrapolation of the data of Fig. 4 to zero H_2 gives a value of $P\tau^{-1} = 3\,(+4, -2) \times 10^{-4}$ μsec-Torr, which when attributed to the 0.02% HF concentration, results in a value of $P_{HF}\tau^{-1} = 1.5\,(+2, -1)$ μsec-Torr^{-1}. This value, although imprecise, is in agreement with the value of 1.6 μsec-Torr^{-1} obtained by Osgood, Sackett, and Javan.[9] When no H_2 was in the gas mixture, a somewhat slower decay rate was measured, indicating some contribution from the back reaction of Reaction (6). The slope of the data in Fig. 4 represents the value of $k_4(3)$, or more precisely, the sum of $k_4(3)$ and the rates of any multiquantum transfers as well as any V-R, T deactivations of HF(3) by H_2.

With any V-R, T contributions neglected and single-quantum exchanges assumed, the exothermic exchange rates $k_{-4}(v)$ were calculated from the measured rates $k_4(v)$ and the equilibrium constant for the process. These exothermic exchange rates increase with v in the ratio of 1, 1.9, and 4.0

for $v = 1$, 2, and 3, respectively. The rates for energy exchange between harmonic oscillators having no energy mismatch, $\Delta E(v) = 0$, would scale with v as 1, 2, and 3. However, HF is anharmonic, and the energy mismatches increase with the vibrational level. Despite these differences, the scaling of the rates does not differ greatly from the theoretical scaling for harmonic oscillators.

B. **VIBRATIONAL RELAXATION OF HF(v = 1, 2, AND 3) IN N_2**

The relaxation times of HF($v = 3$) in N_2 were measured for various partial fractions of HF. These data are listed in Table II and plotted in Fig. 7. The total pressure of the gas sample was varied so that the partial pressure of HF remained 4 mTorr for most of the experiments. Data obtained in experiments conducted with 2, 8, and 20 mTorr of HF were essentially unchanged from the 4-mTorr data. Only a few experiments were performed for HF($v = 1$ and 2) deactivation by N_2; these results are also listed in Table II. The value of the deactivation rate for HF($v = 1$)-N_2 was determined to be $(1.45 \pm 0.2) \times 10^{-4}$ μsec-Torr^{-1}. This value compares favorably with the values of $(1.52 \pm 0.15) \times 10^{-4}$ and $(1.25 \pm 0.6) \times 10^{-4}$ μsec-Torr^{-1} obtained in the more extensive studies by Bott and Cohen[12] and Hancock and Green,[15] respectively.

The deactivation rates for HF($v = 1$, 2, and 3)-N_2 listed in Table III indicate that the rate increases rapidly with increases in v. The ratio of the rate for HF($v = 3$) to that for HF($v = 1$) is a factor of 20, whereas that for resonant harmonic oscillators is a factor of 3. One of the reasons for this rate increase with v is that the energy defects, $\Delta E(v)$, for the high vibrational levels are
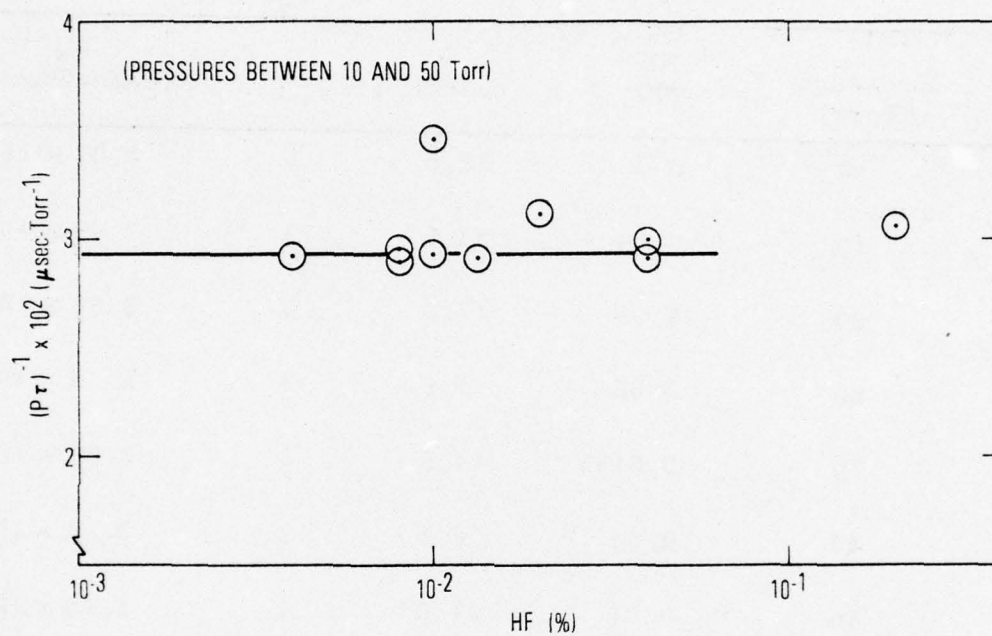
(PRESSURES BETWEEN 10 AND 50 Torr)

Fig. 7.   Deactivation Rates of HF(v = 3) in N_2 for
Various Amounts of HF

TABLE II. VIBRATIONAL RELAXATION DATA FOR HF(v = 1, 2, AND 3) IN N_2

Data	Pressure (Torr)	HF (%)	τ (μsec)	v	P_τ^{-1} (μsec-Torr^{-1})
1	10	0.2	32.6	3	3.07×10^{-3}
2	10	0.04	33.5	3	2.99×10^{-3}
3	20	0.04	17.3	3	2.89×10^{-3}
4	20	0.02	15.9	3	3.14×10^{-3}
5	30	0.0133	11.5	3	2.89×10^{-3}
6	40	0.01	8.6	3	2.92×10^{-3}
7	10	0.01	29.0	3	3.45×10^{-3}
8	50	0.008	7.0	3	2.86×10^{-3}
9	50	0.008	7.0	3	2.86×10^{-3}
10	25	0.008	13.6	3	2.94×10^{-3}
11	50	0.004	6.9	3	2.90×10^{-3}
12	100	0.004	12.3	2	8.1×10^{-4}
13	100	0.004	12.5	2	8.0×10^{-4}
14	99	0.004	70.0	1	1.44×10^{-4}
15	99	0.004	69.0	1	1.47×10^{-4}

AVERAGE VALUES: v = 1 1.45×10^{-4} v = 3 2.92×10^{-3}

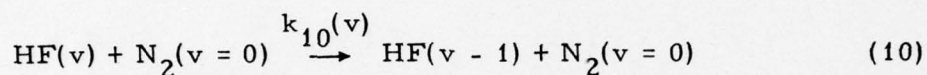   v = 2 8.1×10^{-4}

TABLE III.   RELAXATION RATES OF HF(v = 1, 2, AND 3) IN N_2

v	$\Delta E(v)$ (cm^{-1})	$k_9(v)$ (μsec-Torr^{-1})	$k_9(v)/k_9(1)$
1	1628	1.45×10^{-4}	1
2	1462	8.1×10^{-4}	5.6
3	1294	2.92×10^{-3}	20

small since HF is very anharmonic. The energy defects are listed in Table III for the exchanges

$$HF(v) + N_2(v = 0) \overset{k_9(v)}{\rightleftharpoons} HF(v - 1) + N_2(v = 1) + E(v) \tag{9}$$

The V-R, T deactivation process

$$HF(v) + N_2(v = 0) \overset{k_{10}(v)}{\longrightarrow} HF(v - 1) + N_2(v = 0) \tag{10}$$
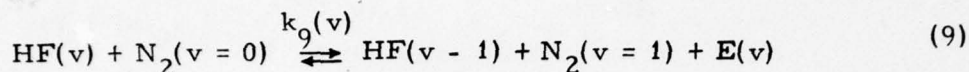
is most likely a small contribution to the total deactivation because V-R, T deactivation requires the conversion of a whole quantum of vibrational energy to rotational, translational energy instead of the smaller energies, $\Delta E(v)$, of the V-V exchanges. Possible multiquantum exchanges could require even smaller amounts of energy to be converted to rotational, translational energy.

C. VIBRATIONAL RELAXATION OF HF(v = 1, 2, AND 3) IN CO_2

The relaxation rates obtained for HF(v = 2) and HF(v = 3) in various mixtures of CO_2 are plotted in Fig. 8; the rates for HF(v = 1) are plotted in Fig. 9. Relaxation times were also calculated from the rise times and decay times of the CO_2 fluorescence at 4.2 μm. It is more difficult to determine rise times than decay times because of the necessity of extrapolating the slowly decaying part of the trace to time equal zero. Therefore, the rise-time data showed more scatter but were in agreement with the data obtained from the decaying HF(v = 1) fluorescence signals. The relaxation rates of Figs. 8 and 9 were extrapolated to 100% CO_2 and are listed in Table IV along with the results of previous studies. A rate for HF(v = 3)-CO_2 somewhat faster ($\sim \times 1.55$) than that reported by Airey and Smith[5] was obtained, but the values
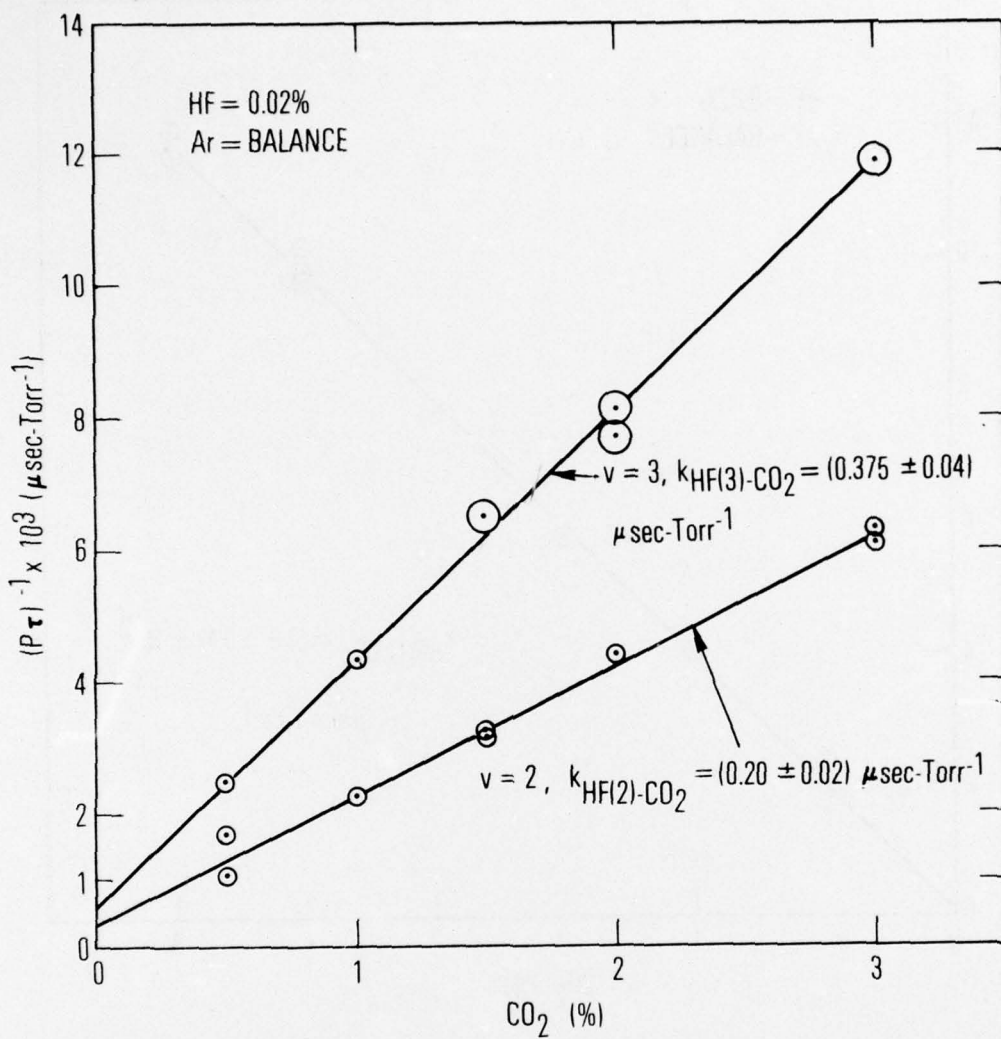
-22-

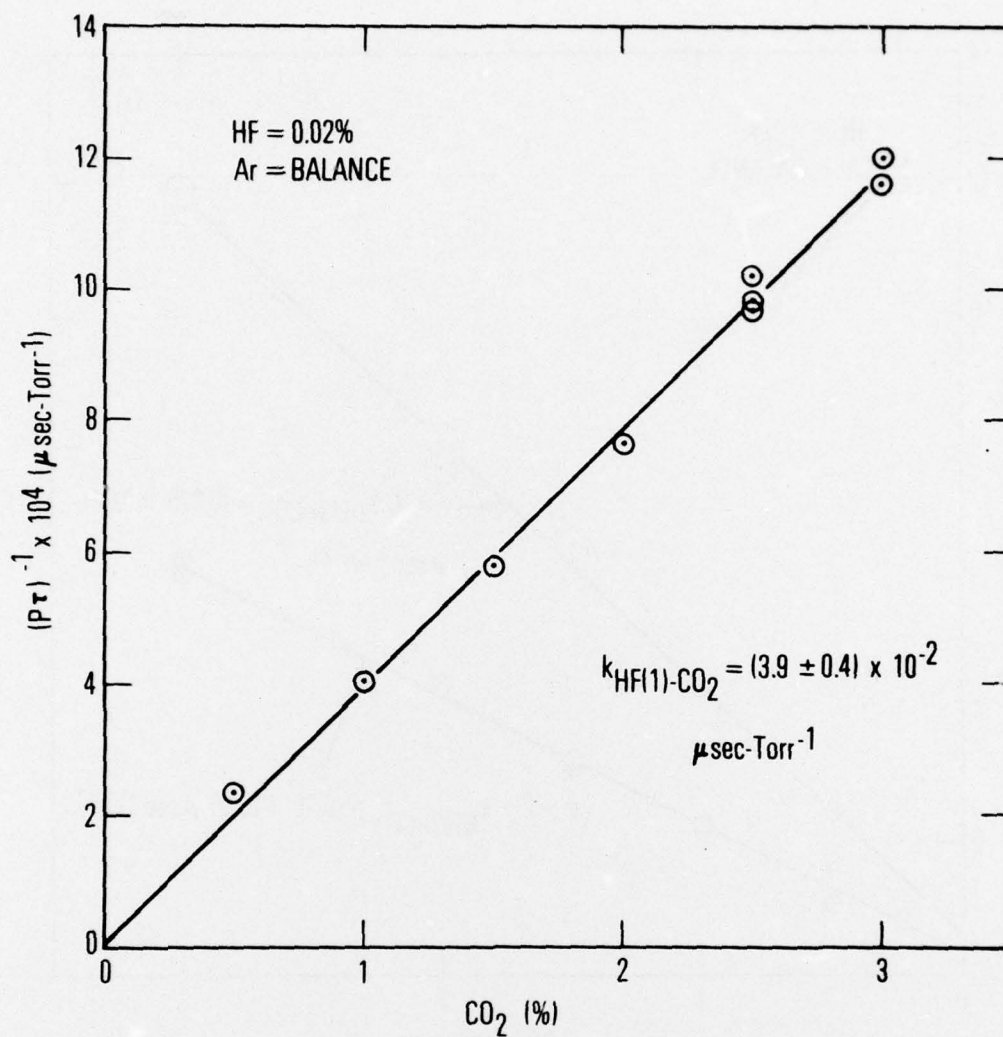Fig. 8. Deactivation Rates of HF($v = 3$) and HF($v = 2$) in Mixtures Containing Various Amounts of CO_2

Fig. 9. Deactivation Rates of HF(v = 1) in Mixtures Containing Various Amounts of CO_2

TABLE IV.   RELAXATION RATES OF HF(v = 1, 2, AND 3) IN CO_2

Reference	k_{11} (μsec-Torr^{-1})		
	HF(v = 1)	HF(v = 2)	HF(v = 3)
Airey and Smith[5]	0.040	0.16	0.24
Hancock and Green[14]	0.059		
Bott and Cohen[2]	0.036		
Lucht and Cool[17]	0.041		
Kwok and Cohen[8]	0.041	0.16	0.16
Kwok[18]			0.37
This study	0.039 ± 0.004	0.20 ± 0.02	0.375 ± 0.04

for the $v = 1$ and 2 exchanges are in very good agreement. The HF($v = 3$) rate agrees with a measurement by Kwok.[18] The present value of the HF($v = 1$)-CO_2 relaxation rate, 0.039 ± 0.004 µsec-Torr^{-1}, is also in good agreement with the values reported by the other investigators.

Stephens and Cool[19] concluded that the deactivation of HF($v = 1$) proceeds primarily by the exchange

$$HF(v) + CO_2(00°0) \rightleftharpoons HF(v - 1) + CO_2(00°1) + \Delta E = 1612 \text{ cm}^{-1} \quad (11)$$
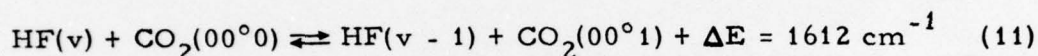
This conclusion was based on the behavior of their CO_2 fluorescence profiles and the experimental results of Hancock and Green.[15] The good agreement of the calculated values of Dillon and Stephenson[11] with the experimental values of Airey and Smith[5] and the present study seem to substantiate this conclusion.

D.   <u>VIBRATIONAL RELAXATION OF HF($v = 3$) BY O_2</u>

The relaxation rates of HF($v = 3$) in O_2 are shown in Fig. 10 for various partial fractions of HF. The slope of the data indicates a rate of $(7.5 \pm 1) \times 10^{-4}$ µsec-Torr^{-1} for the deactivation of HF($v = 3$) by O_2. This rate is 16.7 times faster than the value of 0.45×10^{-4} obtained[12] for HF($v = 1$) deactivation by O_2. However, the rate quoted for HF($v = 1$) deactivation by O_2 is an upper limit[12] because of its small value (the presence of 3 ppm of H_2O in the O_2 could have contributed 0.12×10^{-4} µsec-Torr^{-1} to the measured value). The increase in the rate for HF($v = 3$) over that for HF($v = 1$) in O_2 is similar to that observed for HF(v) in N_2. Because of this similarity, it was presumed that the nearly resonant process
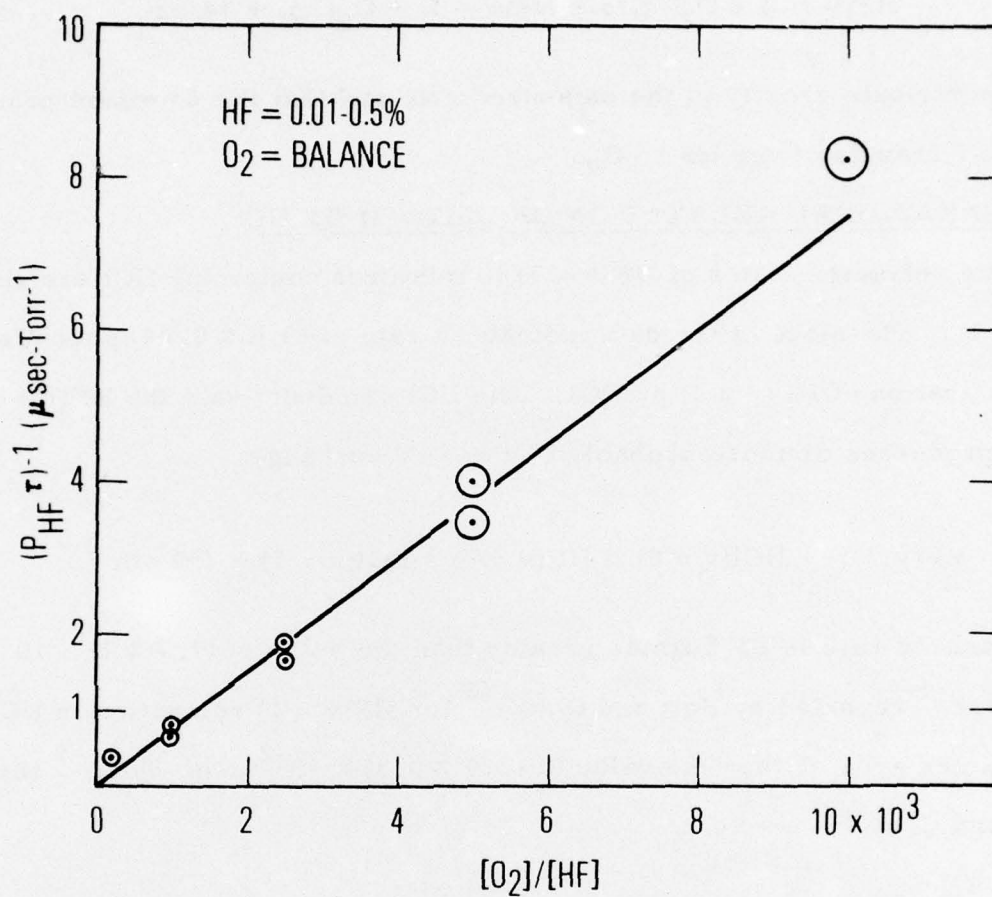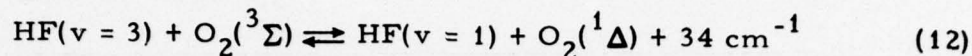
-26-

Fig. 10. Deactivation Rates of HF(v = 3) in O_2

$$HF(v = 3) + O_2(^3\Sigma) \rightleftharpoons HF(v = 1) + O_2(^1\Delta) + 34 \text{ cm}^{-1} \qquad (12)$$

did not contribute greatly to the measured rate and that the dominant process is the V-V transfer from HF to O_2.

E. VIBRATIONAL RELAXATION OF HF(v = 3) BY HCl

The relaxation rates of HF(v = 3) in mixtures containing HCl are shown in Fig. 11. The slope of the data indicates a rate of (0.4 ± 0.04) μsec-Torr^{-1} for deactivation of HF(v = 3) by HCl. The HCl can deactivate the HF(v = 3) by V-R, T processes or more probably by the V-V exchange

$$HF(v = 3) + HCl(v = 0) \rightleftharpoons HF(v = 2) + HCl(v = 1) + 739 \text{ cm}^{-1} \qquad (13)$$
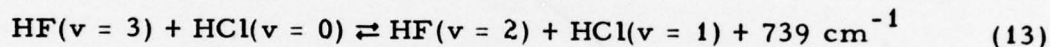
The measured rate is 23.5 times greater than the value of $(1.7 \pm 1) \times 10^{-2}$ μsec-Torr^{-1} reported by Bott and Cohen[12] for HF(v = 1) relaxation in HCl and 14 times greater than the value of $(2.9 \pm 0.3) \times 10^{-2}$ μsec-Torr^{-1} reported by Ahl and Cool.[20]
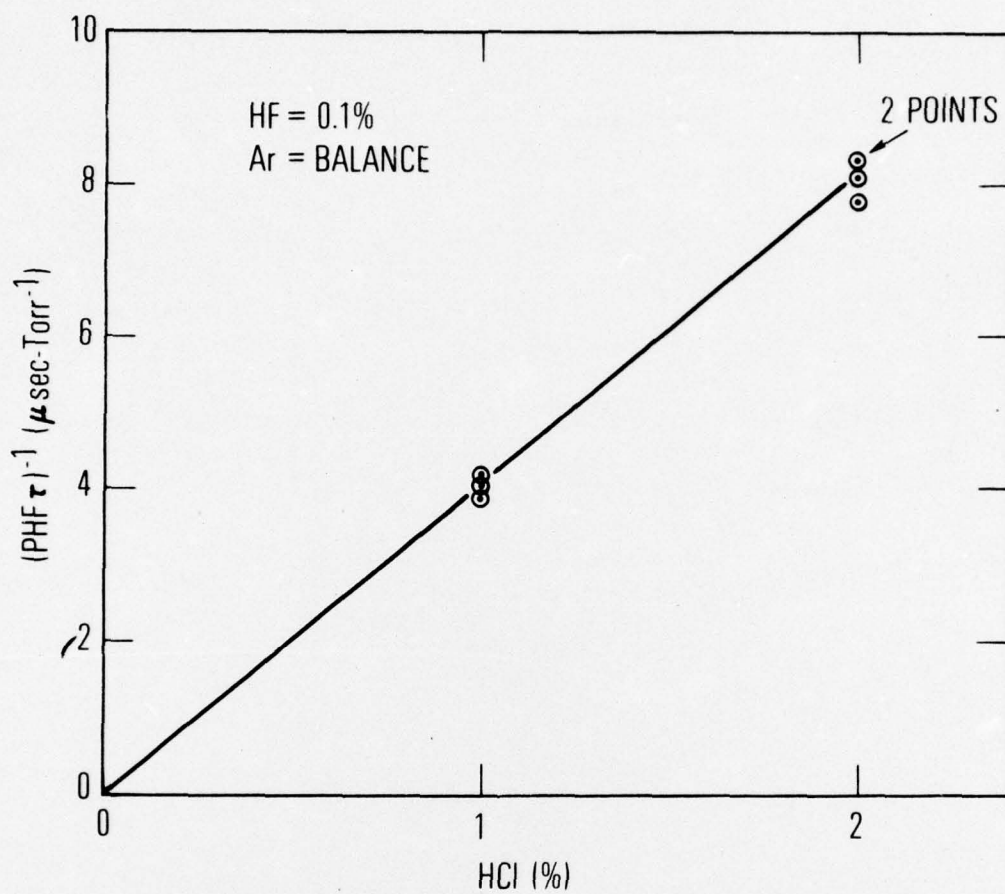
Fig. 11.   Deactivation Rates of HF(v = 3) in Mixtures
Containing Various Amounts of HCl

IV. DISCUSSION

The rates obtained for $HF(v)$-CO_2 are in good agreement with the experimental values of Airey and Smith[5] and Kwok.[18] The v dependence is in reasonable agreement with the theoretical calculations of Dillon and Stephenson.[11] The agreement of the $HF(v)$-CO_2 experimental data serves as a check on the several different methods for measuring upper vibrational level deactivation rates. The present technique provides data that are easy to interpret and has advantages over the other methods. It could possibly be extended to higher vibrational levels by the use of a fuel other than H_2, e.g., HBr or HI, in the chemical laser.

The rates of vibrational energy transfer from the upper vibrational levels of HF to N_2, O_2, HCl, and CO_2 increase faster with v than the predicted rates for harmonic oscillators having no energy defect. Part of this increase can be attributed to the decrease of the energy defect, $\Delta E(v)$, with v so that less energy must be absorbed by the rotational and translational degrees of freedom for the transfer of a quantum of energy. However, the dependence of the rates on v can be explained only qualitatively in terms of the anharmonicity of HF and the resulting energy defect dependence on v. The probabilities for V-V exchanges between $HF(v = 1)$ and homonuclear diatomic molecules are plotted versus energy defect in Fig. 12 of Ref. 12. They decrease by a factor of 3 with each increase of 334 cm^{-1} in the energy defect. Since the energy defect for an HF $3 \rightarrow 2$ transition is smaller than that for an HF $1 \rightarrow 0$ transition by 334 cm^{-1}, the exchange rates for $HF(v = 3)$ could be expected

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to be faster than those for HF(v = 1) by a factor of 3 if energy defects were the only consideration. The rates could be expected to increase a factor of $3 (k \propto v)$ even if the molecules behaved as harmonic oscillators so that a factor of 9 increase in the rates might be anticipated. However, the measured rates for HF(v = 3) were 20 ± 4 times greater than those for HF(v = 1) in N_2, O_2, and HCl, or approximately 2.2 times faster than this estimate of a factor of 9.

The V-V exchange between HF(v) and H_2 described by Process (4) is endothermic. However, the reverse exothermic exchanges calculated from the measured rates scaled as 1, 2, and 4 for v = 1, 2, and 3. The energy defect for HF(3) exchange with H_2 is 334 cm^{-1} larger than that for HF(v = 1), whereas the energy defect for HF(3) exchange with N_2, O_2, and HCl is 334 cm^{-1} less than that for HF(1). This difference may explain qualitatively, although not quantitatively, the weaker v dependence of the HF(v)-H_2 rates.

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